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Effects of oil type on the properties of short oil alkyd coating materials

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Abstract−Short-oil alkyd resins were prepared by using five different oil types: corn oil, rice bran oil, sunflower oil, soya bean oil and dehydrated castor oil (DCO). Among these, soya bean oil gave alkyd resin with the darkest color because oxidation occurred. Auto air-dried coating films were developed and it was shown that film prepared from rice bran oil-based alkyd exhibited the longest drying time due to the low number of double bonds compared to other and the extra natural antioxidant in rice bran oil. DCO alkyd-based film revealed the shortest drying time, the greatest hardness but the poorest alkali and sea-water resistance. This is caused by the differences in the type of fatty acid and double bonds, the high amount of double bonds being in DCO. In addition, an increase in the reaction temperature only had an influence on darkening the alkyd color and decreasing the drying time of coating films. In terms of technical properties and cost competitiveness, soya bean oil-based film is the best. Coating films derived from all oil-based alkyds, except DCO, look promising for use in surfboard manufacturing.

Key words: Alkyd Resin, Polyester Coating, Film Properties

INTRODUCTION

Polyester coating material, or alkyd, is widely used for surface coating as binders, adhesives and plasticizers. It is produced from polyols, dibasic and fatty acid or oils by condensation polymerization [Parsons, 1993]. Alkyd is of interest since it tends to be the lowest in cost among the coating materials and tends to give a coating that exhibits fewer film defects during applications. On the other hand, durability of alkyd films, especially for outdoors use, tends to be poorer than films, i.e., acrylics and polyurethanes [Zeno et al., 1996; Kim et al., 2003]. However, one of the factors affecting coating film properties is the type of fatty acid or oil used in the alkyd production [Kabasakal et al., 1995, 1996]. Various types of oil can result in differences in film properties.

From our study, there is a potential to apply alkyd coating film in sea-water sport equipment, e.g. for windsurfing and surfboarding. The objective of the present work was, then, to develop alkyd coating films with good sea-water resistance for being applied in windsurf manufacturing. The effects of various domestic oils on the characteristics and properties of the alkyd resin and coating film properties were investigated. Our preliminary investigation revealed that domestic oils that are suitable for producing alkyds to form clear films via auto air drying are corn oil, rice bran oil, sunflower oil, soya bean oil, and dehydrated castor oil (DCO).

EXPERIMENTAL

1. Materials

The above five types of oil were supplied from local industries and the characteristics and price of the oil were as listed in Table 1. The acid value and iodine value of oil were determined according to ASTM D1639 and ASTM D1959, respectively. The acid value was defined as the amount (mg) of KOH required to neutralize the free fatty acid in 1 g of oil. In brief, 5 g of oil was dissolved in 100 ml of neutral solvent mixture of isopropanol and toluene (1 : 1 by volume). The solution was titrated with 0.1 N standard solution of potassium hydroxide in methanol with phenolphthalein as an indicator. The iodine number of oil was determined as the number of grams of iodine absorbed or reacted at the double bonds of 100 g of oil. Higher iodine number represented more double bonds in the molecule. The hydroxyl value of oil was a measure of the hydroxyl content reported as the amount (mg) of KOH equivalent to the hydroxyl content in 1 g of oil. The value was obtained from the local supplier determined by ASTM D1957. In terms of price competitiveness, rice barn oil is cheapest while DCO is the most expensive.

Phthalic anhydride and glycerol (commercial grade) were provided by Siam Chemical Industry Coporation. Nitrocellulose (RS type, nitrogen content=11.5-12.2% by Dopont Nitrometer test, viscosity (conc.20%)=3-4.9 s) was provided by Nitro Chemical Industry Ltd.

2. Preparation of Short Oil Alkyd

As shown in Table 2, short oil length alkyd resins (35% oil length) were formulated by using phthalic anhydride, glycerol and each type of oil.

The mixture of oil, glycerol and catalyst (LiOH), amounting to 0.03% of oil, was heated to a desired temperature and the alcoholysis reaction was conformed at this temperature for one hour to form monoglyceride. The temperature used for alcoholysis reaction was reported in the range of 200-250 °C depending on the types of raw materials. [Erciyes et al., 1993; Kabasakal et al., 1995, 1996]. Our preliminary work has revealed that the appropriate temperature for the alcoholysis reaction of our system should be at 210-230 °C. Lower temperature than 210 °C would result in a very slow reaction. Higher temperature than 230 °C would result in a gel-like solution of which the viscosity was too high to be further used as coating films. Con-

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Table 1. Characteristics and price of oils used in this work

Type of oil	Acid value (mg KOH/g oil)	Iodine value (g I_2/100 g oil)	Hydroxy value* (mg KOH/g oil)	Linolenic (%wt)	Type of double bond	Local price (US$/liter)
Corn	0.64	120.1	-	0-2	nonconjugated	1.50
Rice bran	0.81	98.3	-	1	nonconjugated	0.85
Sunflower	0.19	124.2	-	2	nonconjugated	1.00
Soya bean	0.11	120.0	-	5-11	nonconjugated	0.90
DCO	1.8	132.2	12.7	0	conjugated	2.50

*Obtained from the local supplier determined by ASTM 1957.

Table 2. Formulation of short oil alkyd

Ingredient	Composition (% by weight)
Phthalic anhydride	40.8
Oil	33.3
Glycerol	25.9

sequently, the desired temperatures of 210 °C and 230 °C were selected in this study. Monoglyceride formed could be tested by dissolving obtained resin in ethanol (1 : 3 by weight) to form clear solution at room temperature [Edward, 2001]. After that, the phthalic anhydride was added and the esterification reaction was carried out at the same temperature for 5 hr. At each hourly interval of reaction, the characteristics of the resin such as acid number [ASTM D1639], viscosity and color [ASTM D1544] were determined.

3. Preparation and Properties of Coating Film

To produce a coating film, nitrocellulose was added to the obtained resin (45 : 55 by weight). The film with the thickness of 60 μm was cast on different substrate depending on the property tests required. For the drying time [ASTM D1640] and gloss test [ASTM D523], a glass plate was used as substrate. For hardness [Thai Industrial Standards 285], water [ASTM D3359], acid [ASTM D3359] and sea-water resistance test, a tin plate was used. Mild steel was used as substrate for the adhesion test [ASTM D1647], while glass tubes were used for alkali test [ASTM D3359].

Water, sea-water and acid resistance tests were performed at room temperature by immersing the film in distilled water, local sea-water and 5% sulfuric acid for 48 hr, respectively. For alkali resistance test, 5% sodium hydroxide was used for 24 hr immersion.

Visual observation was carried out in all cases to search for appearance of blisters or any physical damage. After the completion of the specified duration tests, the film was removed and the surface was observed for any sign of corrosion. Properties of coating film from commercial short oil alkyd were determined and compared with various oil-based coating films.

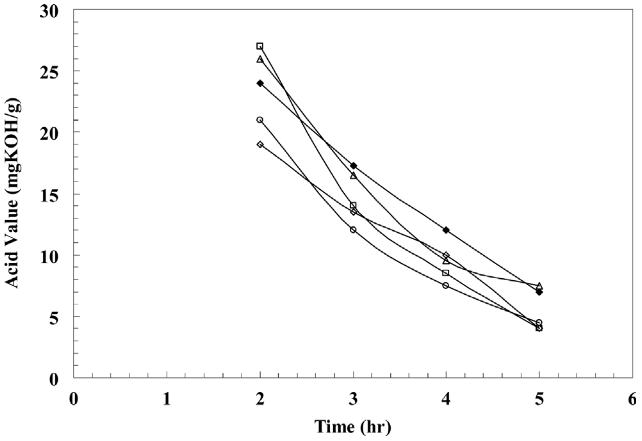

Fig. 1. Acid values of alkyd resins produced from various oils at 210 °C: (◇) Corn oil, (□) Rice oil, (△) Sunflower oil, (○) Soya bean oil, (◆) DCO.

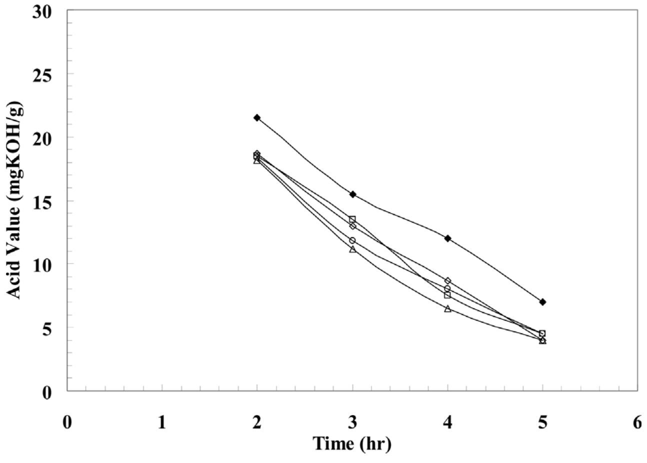

Fig. 2. Acid values of alkyd resins produced from various oils at 230 °C: (◇) Corn oil, (□) Rice oil, (△) Sunflower oil, (○) Soya bean oil, (◆) DCO.

RESULTS AND DISCUSSION

1. Acid Values of Alkyd Resins

Figs. 1 and 2 present the acid values of alkyd resins synthesized at 210 °C and 230 °C, respectively. The acid values of the resins were continuously decreased as reaction time increased. The decrease of acid values resulted from the proceeding of the esterification between monoglyceride and phthalic anhydride. When the reaction was stopped at 5 hr, the acid values of all alkyd resins from the five oil types were more or less the same and lower than 10, thereby passing the Thai Industrial Standards.

Considering the decreaseing rate of acid value, it can be seen that the acid value of DCO alkyd resin tended to decrease more slowly compared to other oil-based alkyd resins. As a result, DCO alkyd resin has the highest acid value at 5 hr of reaction. This could be caused by the highest amount of free acid in pure DCO (see Table

1). Considering the effects of increased reaction temperature on the acid value, it could be noticed that when the temperature was increased from 210 °C to 230 °C, the acid value of the resin at the end of 2 hours of reaction became lower. This implied a higher rate of esterification during the first two hours, after which an increase in the reaction temperature had no effect on the rate of esterification.

Alkyds synthesized from various oils were compared to a commercial resin, and it was found that the acid values of alkyds synthesized were similar to that of a commercial resin (7.05) and all of them conformed to the Thai Industrial Standards (see Table 3).

Table 3. Short oil alkyd specifications of Thai Industry Standards

Specification	Thai industrial standard
Oil (%)	>32
Phthalic anhydride, PA (%)	>38
Acid value (mgKOH/g)	<10
Viscocity$\times 10^{-3}$ (Pa·s) (60%NVM)	<6340
Color (Gardner)	<7
% Nonvolatile, %NVM	60±1
Drying time (min)	N/A

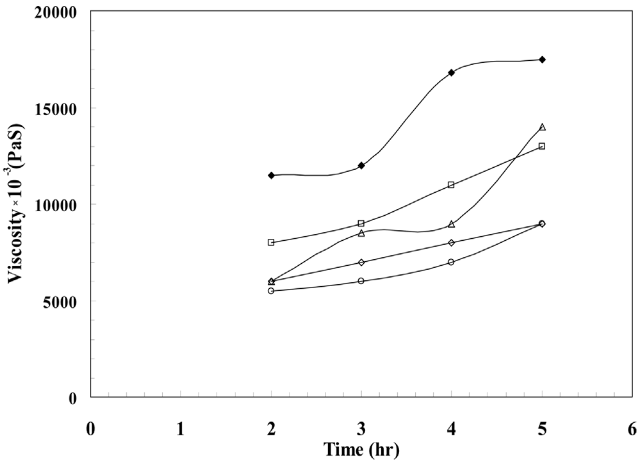

Fig. 3. Viscosities of short oil alkyd resins produced from various oils at 210 °C: (◇) Corn oil, (□) Rice oil, (△) Sunflower oil, (○) Soya bean oil, (◆) DCO.

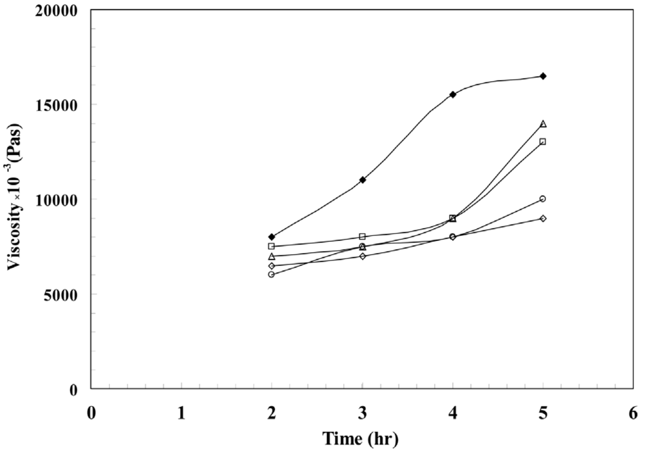

Fig. 4. Viscosities of short oil alkyd resins produced from various oils at 230 °C: (◇) Corn oil, (□) Rice oil, (△) Sunflower oil, (○) Soya bean oil, (◆) DCO.

2. Viscosity of Alkyd Resins

Figs. 3 and 4 depict the viscosity of alkyd resins containing 70% nonvolatile at 210 °C and 230 °C, respectively. It can be observed that the viscosity of alkyd resins was increased as the reaction time increased for all oil types. During the first 2-3 hr of reaction, the viscosity was slowly increased. After that the viscosity was significantly increased as the esterification between monoglyceride and phthalic anhydride continued. However, the reaction came to a stop after 5 hr since alkyd resins obtained after 5 hr were very viscous and some started to gel due to the occurrence of chain polymerization [Parsons, 1993]. The results on the viscosity corresponded to the acid value results reported earlier.

Comparing the oil types, the viscosity of the DCO alkyd resin was the highest. This might be attributed to the linoleic conjugated double bonds in the structure of the DCO which were not found in the other oils. Fatty acids with conjugated double bonds can be dimerized more rapidly than those with nonconjugated bonds, and dimerization rate increases with the level of unsaturation [Parsons, 1993]. As a result, the macromolecules of the DCO alkyd resin formed should be more massive than those of other oil-based resins, thereby resulting in the highest viscosity.

Comparing Fig. 3 to Fig. 4, increasing the reaction temperature from 210 °C to 230 °C had no influence on the final viscosity of the alkyd resin. The viscosity of alkyds synthesized at 5 hr of reaction was also similar to a commercial resin (12.20 Pa·s). However, it was noted that after 2 hr of reaction the initial viscosity at 230 °C seemed to be similar to that synthesized at 210 °C, or in the case of DCO it was slightly lower. This might be due to the occurrence of the side reaction between the hydroxy groups in DCO at high temperature along with the esterification reaction. This would result in a decrease in the viscosity at high temperature, which was inconsistent to a decrease in acid values presented in the previous section. For a longer reaction time, more alkyd was produced and less side reaction would occur resulting in an increase in the viscosity and a decrease in the acid values.

3. Color of Alkyd Resins

The color of the alkyd resin solution was evaluated by means of comparison to standard solution colors ranging from 1 to 18 (Gard-

Table 4. Color of alkyd resin synthesized from various oils at 210 °C and 230 °C

Type of oil	Gardner color scale of resins synthesized at two reaction temperatures	
	210 °C	230 °C
Corn	4-5	12-13
Rice bran	9-10	10-11
Sunflower	5-6	10-11
Soya bean	10-11	11-12
DCO	6-7	14-15
Commercial resin	4-5*	
Thai Industry Standard	10 Max*	

*Unknown temperature

ner color). A higher value indicates a darker yellow while a lower value indicates a lighter yellow.

The results presented in Table 4 on the color of the alkyd resin synthesized at 210 °C from various oils showed that the colors of the alkyd resins were different depending on the oil used. Soya bean oil gave the darkest yellow alkyd due to a high amount of linolenic acid (5-11%) in soya bean oil [Parsons, 1993]. On the other hand, the color of corn oil based alkyd resin was lightest due to the low amount of linolenic acid (0-2%) in the corn oil.

Besides, the color of alkyd resin also depended on the temperature of reaction. At higher reaction temperature (230 °C for this case), the synthesized alkyd was darker than the one obtained at lower temperature (210 °C). This could be caused by the more oxidation reaction occurring at higher temperature. The oxidation reaction could have been occurring on the double bonds of natural oils represented in terms of iodine value. Consequently, DCO and rice bran oil which had the highest and lowest iodine values (Table 1) rendered the darkest and lightest yellow alkyds produced at 230 °C, respectively. Moreover, the type of conjugated double bonds in the DCO structure could also contribute in the darkest color of DCO alkyd.

The causes of the darkness of alkyd synthesized were worth exploring. Possible factors could be the amount of catalysts used, the severity of esterification and the occurrence of oxidation reaction. Additional experiments using soya bean and corn oils have verified that reducing the amount of catalysts used (batch nos. 2 and 6 in Table 5), and decreasing the temperature of monoglyceride to 180 °C before adding phthalic anhydride (batch no. 3 in Table 5) had no effects on the color of alkyd resins obtained. The occurrence of oxidation in the presence of oxygen during alcoholysis and esterification has proven to be the main cause of the dark alkyd resins synthesized. Results of batch nos. 4 and 7 in Table 5 show that, when nitrogen was introduced into the solution during the synthesis at 210 °C, the colors of the corn oil and soya bean oil-based alkyd resins obtained were clearer than their synthesized counterparts when nitrogen only covered the solution surface (batch nos. 1 and 5).

Alkyd synthesized from soya bean oil was compared with the commercial resin. It could be seen that the color was similar. In addition, the colors of the alkyd resins synthesized from various oils conformed to the Thai Industrial Standards.

4. Drying Time of Coating Films

Short oil alkyds developed from various oils were not self air-drying due to the low level of unsaturated oil. Nevertheless, it can be rendered auto air-drying film by mixing with nitrocellulose. The presence of nitrocellulose varnishes renders good drying [Paul, 1996].

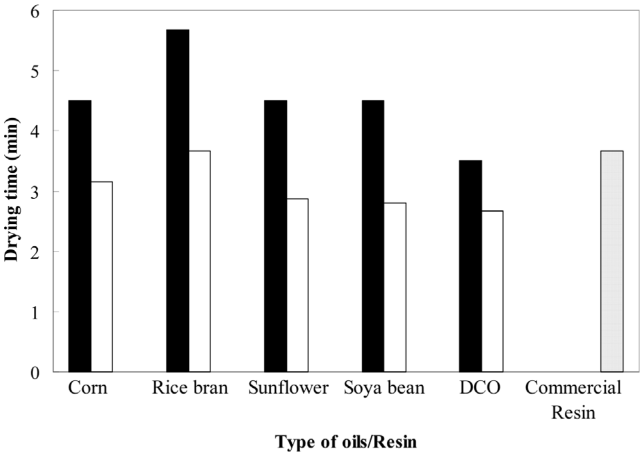

Fig. 5. Effects of oil types and reaction temperature on the drying time of short oil alkyd films: (■) 210 °C, (□) 230 °C, (▦) Commercial resin.

From Fig. 5, at each reaction temperature, coating film from short oil DCO alkyd resin showed the shortest drying time. This might be due to the occurrence of higher degree of reaction from the conjugated double bonds in DCO and also the greater amount of double bonds than other oils so it can be oxidized better than the others. Therefore, DCO oil-based film had shorter drying time than films from the other oils.

The drying times of corn oil, sunflower oil and soya bean oil derived films were similar since the amounts of nonconjugated bonds in the oil structure were similar [Parsons, 1993] (see the iodine values in Table 1). Drying time of rice bran oil film was higher than other oils since there were fewer double bonds in rice bran oil than other oils. Moreover, rice bran oil contains a natural antioxidant called oryzanol which cannot be found in other oils [Xu and Godber, 2001]. Therefore, the oxidation rate of rice bran oil was not as high as the others. Film from the commercial alkyd resin mixed with nitrocellulose could also be dried within the same range of the drying time of our films.

When the reaction temperature was elevated, the drying times of the films tended to decrease because of an increase in chain growth

Table 5. Comparison of alkyd resin synthesized at 210 °C for 5 hr

Oils	Batch no.	Amount of catalyst (% of oil weight)	Acid values (mgKOH/g)	Viscosity $\times 10^{-3}$ (Pa·s)	Color (Gardner scale)
Soya bean oil	1	0.030	3.30	9140	10-11
	2	0.015	2.98	10400	10-11
	3	0.015	3.10	9850	10-11^a
	4	0.015	2.37	10000	5-6^b
Corn oil	5	0.030	5.20	9150	4-5
	6	0.015	5.23	10200	4-5
	7	0.015	5.17	9820	3-4^b

Note: (a) Reduce the temperature of monoglyceride to 180 °C before adding phthalic anhydride. (b) Reduce the temperature of monoglyceride to 180 °C before adding phthalic anhydride and nitrogen was introduced into the solution.

Table 6. Property comparison of films derived from various short oil alkyd resins from the synthesis temperature of 210 °C and 230 °C and the commercial alkyd

Type of oil	Hardness[a] (g)	Resistance to				Adhesion[b]	Gloss[c]
		water	sea-water	acid	alkali		
Corn	480	///	///	///	//	5B	102.8
Rice bran	470	///	///	///	//	5B	103.2
Sunflower	480	///	///	///	//	5B	103.0
Soya bean	470	///	///	///	//	5B	103.1
DCO	900	///	//	///	/	5B	102.6
Commercial resin	1000	///	//	///	/	5B	102.8

Note: ///=excellent, //=good, /=fair. (a) Mechanical scratch test by Sheen instrument Ltd. (b) 5B=excellent adhesion. (c) 102-103=fair gloss.

polymerization [Parsons, 1993; Paul, 1996].

5. Hardness of Coating Films

It is known that the ring structure of phthalic anhydride helps improve the hardness of the coating film. Since the amounts of phthalic anhydride used in alkyd production from various oils were similar (see Figs. 1 and 2) and because of the similarity in the nonconjugated double bonds of corn, rice bran, sunflower and soya bean oils, the hardness of the various oil-based films, except DCO, was essentially the same (see Table 6). Among the five types of oil-based films, the hardness of the DCO film was the highest. This could be attributed to the fact that the macromolecules of the DCO alkyd resin formed were more complex than those of the other oil-based resins due to the presence of hydroxyl groups in the recinoleic acid of the DCO oil. Furthermore, the hydroxyl groups of the recinoleic acid could readily blend with the nitrocellulose because of its high degree of polarity [Paul, 1996], thereby forming the hardest DCO-based coating film compared to the other oil-based films.

An increase in the reaction temperature had no effect on the hardness of films as the amount of phthalic anhydride used was similar.

Alkyds synthesized from various oils were compared to the commercial resin. It could be seen that a commercial resin film was harder than those from our alkyd resins. This could be due to the use of alcohol mixture such as glycerol and pentaerythitol in the commercial resin production. Such an alcohol mixture has more hydroxy groups, compared to pure glycerol, resulting in a more complicated resin network and a harder coating film.

6. Water, Sea-water, Acid and Alkali Resistance of Coating Films

Table 6 reveals that water and acid resistances of all oil-based films and the film from the commercial resin were excellent. All films did not show any change after the completion of the test. The sea-water resistance of all oil-based films, except DCO, was also excellent. DCO film became yellow after 48 hr in sea-water immersion, same as commercial resin. The alkali resistance of all oil-based films was relatively poorer than the water, sea-water and acid resistance. Moreover, the alkali resistance of the DCO coating film was the poorest. The poor alkali resistance of DCO-based film corresponded with the high acid value contained in DCO oil. Therefore, NaOH solution could effectively react with free acid residue in DCO-based film. The alkali resistance of all oil-based films of alkyd synthesized from various oils was compared with the commercial resin. It was noticed that the alkali resistance of alkyd synthesized from various oils, except DCO, was better than that of commercial resin.

In addition, increasing reaction temperature had no effects on water, sea-water, acid and alkali resistance of the coating films.

7. Adhesion and Gloss of Coating Films

From Table 6, the adhesion and gloss of all oil-based film and commercial resin film were very similar. Adhesion and gloss of coating film did not depend on types of oil. Besides, reaction temperature had no effects on adhesion and gloss of the coating film.

CONCLUSIONS

Short oil-modified alkyd resins developed from various oil types can be obtained. The color of soya bean alkyd resin was the darkest yellow. The dark color of resins, mainly caused from oxidation during esterification reaction, can be clearer by purging nitrogen into the solution during the synthesis. Polyester coated films were produced from different oil-based alkyds, except DCO, at the same polymerization conditions such as reaction time, reaction temperature showed similar properties including hardness, water, sea-water, acid and alkali resistance. Rice bran oil-based coating film exhibited the longest drying time due to the low number of double bonds and the extra natural antioxidant called oryzanol in rice bran oil. The DCO-based coating film revealed the shortest drying time, highest hardness but poorest sea-water and alkali resistance, compared to other oils-based films. Increasing reaction temperature from 210 °C to 230 °C darkened the color of alkyd resin and decreased the drying time of coating film but had no effects on the hardness, water, sea-water, acid and alkali resistance, adhesion and gloss of coating films. The performance of the resin and the film was found to be comparable to a commercial resin approved by Thai Industrial Standard. In terms of good technical properties especially sea-water resistance, soya bean oil-based film is the best. However, cost-wise the cost of soya bean oil-based film is slightly higher than rice bran oil-based film. It looks promising that soya bean, rice bran, corn and sunflower oils-based films can be applied for the surfboard manufacturing industry. Further work on the improvement of the hardness of the oil-based films by employing suitable additives will be investigated in order to enhance the performance of the films.

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